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## New Mode of Ion Size Discrimination for Group 2 Metals Using Poly(pyrazolyl)borate Ligands. Control of Stability and Structure of Chelate Complexes by Intra- and InterLigand Contact and Shielding Effect

Yoshiki Sohrin, Masakazu Matsui and Hisao Kokusen\*

Selectivity of  $[\text{HB}(\text{pz})_3]^-$ ,  $[\text{B}(\text{pz})_4]^-$  and  $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]^-$  ( $\text{A}^-$ ;  $\text{pz}$  = 1-pyrazolyl) for group 2 metal ions has been studied by liquid-liquid extraction. Although all the extracted species of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  were distorted octahedral  $\text{A}_2\text{M}$ , the selectivity was highly dependent on the ligand. The steric properties of the ligands and complexes have been elucidated by X-ray diffraction, NMR and molecular mechanics calculations. Poly(pyrazolyl)borates are unusual chelating ligands due to the steric effects.

**Keywords:** Metal ion recognition/ Ligand design/ Liquid-liquid extraction/ X-ray crystallography/ Molecular mechanics

Discrimination of the ion size is an essential factor in ligand design for selective complexation of metal ions. The size distinction with conventional organic ligands is roughly divided into two types [1]. The first is based on the chelate ring size. The chelate ring size is principally determined by the kind and number of atoms, and the order of bonds contained in the ring. For hard metal ions, such as group 2 and lanthanide, the stability constants of conventional chelating complexes decreases gradually with the increase in the ion size. The other type of ion size discrimination is due to the cavity size of macrocyclic ligands. It is especially visible in rigid and

preorganized macrocycles that the most stable complex is formed when the cation diameter matches the cavity size. The type of distinction of ion size more or less restricts the variety of selectivity pattern for ions. The creation of a new mode of ion size discrimination is desirable to produce a novel pattern of ion selectivity and expand the possibility of metal ion recognition.

The coordination chemistry of poly(pyrazolyl)borate ( $\text{A}^-$ ) is being extensively studied [2]. Many unusual features of the ligands are largely derived from their unique structure. All poly(pyrazolyl)borate complexes contain the six membered ring  $\text{RR}'\text{B}(\mu\text{-pz})_2\text{M}$  structure (1), where R and R' can be pz, H, alkyl, aryl, and so forth ( $\text{pz}$  = 1-pyrazolyl). The chelate ring has a boat configu-

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### INTERFACE SCIENCE —Separation Chemistry—

#### Scope of research

The research in the laboratory has been performed in a few years on the design of novel molecular recognition system which is divided into three categories as follows. (i) Design and synthesis of novel ligands with improved stability and separability based on the concept of molecular recognition, and the separation chemistry in the selective metal chelate system employing the new ligands. (ii) Electroanalytical chemistry at liquid-liquid or liquid-membrane interface. (iii) Separation, circulation and biogeochemistry of trace elements in the hydrosphere such as the Pacific Ocean and the Lake Biwa.



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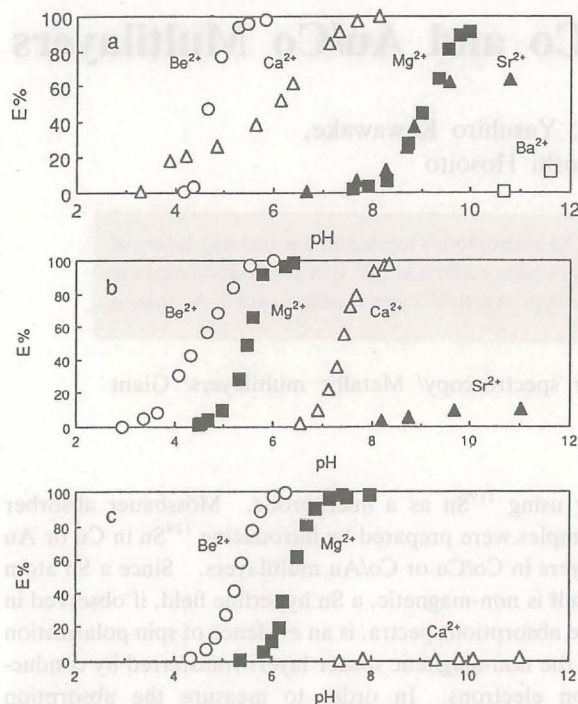
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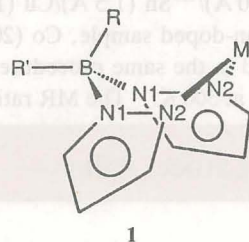
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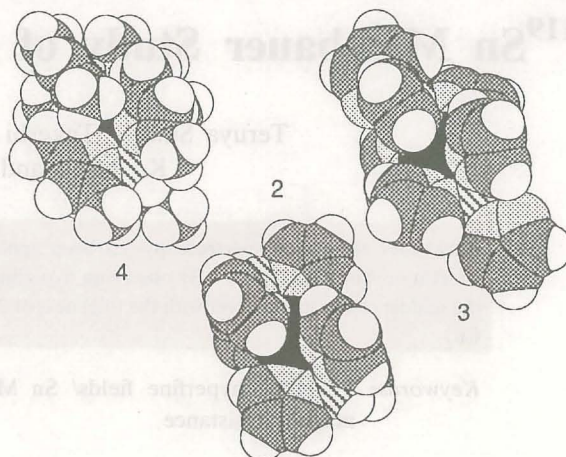
**Figure 1.** Effect of pH on the extraction of group 2 metal ions. Aqueous phase:  $1 \times 10^{-2}$  M KA,  $1 \times 10^{-2}$  M buffer,  $1 \times 10^{-4}$  M  $M^{2+}$  (10 mL). Organic phase: chloroform (10 mL). (a) K[HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>], (b) K[HB(pz)<sub>3</sub>], (c) K[B(pz)<sub>4</sub>].

ration, which enables the R group to approach the metal and bond to it. Trofimenko has termed the ligands "scorpionate," since the ( $\mu$ -pz)<sub>2</sub> moiety looks like claws and the pseudoaxial R group looks like the stinger of the curving tail.



It is fundamentally important in poly(pyrazolyl)borate chemistry to determine how the scorpionate discriminates its prey (metal ion). However, few studies have been reported on the selectivity of the ligands for metal ions and on the stability of their complexes. We have been studying the liquid-liquid extraction of group 2 metal ions with poly(pyrazolyl)borates, and found selectivity trends that are different from conventional chelating ligands [3]. These selectivity trends are derived from the different mode of ion size discrimination.

Figure 1 shows the relationship between extracted percentage of a metal ion (E%) and pH of the aqueous phase. The selectivity pattern is very different depending on the substituents on the ligand molecule. All ligands are tripodal-tridentate and form octahedral A<sub>2</sub>M complexes. The stability of the complexes is



**Figure 2.** Space-filling views of X-ray structure of [HB(pz)<sub>3</sub>]<sub>2</sub>Mg (2), [B(pz)<sub>4</sub>]<sub>2</sub>Mg (3) and [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]<sub>2</sub>Mg (4). The central metals are shown by black balls.

principally responsible for the selectivity. The stability is controlled by the steric effects of the substituents. Because [HB(pz)<sub>3</sub>]<sup>−</sup> has no specific steric effect on formation of the A<sub>2</sub>M complex, its stability decreases in the order Mg<sup>2+</sup> > Ca<sup>2+</sup> > Sr<sup>2+</sup> which is the usual pattern for chelating ligands. The stability for [B(pz)<sub>4</sub>]<sup>−</sup> remarkably drops between Mg<sup>2+</sup> and Ca<sup>2+</sup>. The complex formation with a large metal ion is prohibited by the intraligand contact due to steric crowding around the boron atom (Figure 2). For [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]<sup>−</sup>, methyl groups on the 3-position of the pyrazolyl ring hinder the A<sub>2</sub>M complex formation for small metal ions through the interligand contact, while they stabilize the complex of large metal ions through the shielding effect. As a result, the order of stability is Ca<sup>2+</sup> > Mg<sup>2+</sup> > Sr<sup>2+</sup> > Ba<sup>2+</sup>. These steric factors make [B(pz)<sub>4</sub>]<sup>−</sup> and [HB(3,5-Me<sub>2</sub>pz)<sub>3</sub>]<sup>−</sup> unique ligands in selectivity for the metal ions. It has also been proved that these steric factors produce distinct compositions and structures for Be<sup>2+</sup> complexes.

The results of this work demonstrate a new mode of ion size discrimination by chelating ligands. In this mode, selectivity of ligands for metal ions can be readily changed by introduction of substituents on the ligand. Furthermore, such high selectivity of [B(pz)<sub>4</sub>]<sup>−</sup> for Mg<sup>2+</sup> over Ca<sup>2+</sup> has not been attained by conventional chelating ligands.

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